Russian Journal of Organic Chemistry, Vol. 38, No. 5, 2002, pp. 692–698. Translated from Zhurnal Organicheskoi Khimii, Vol. 38, No. 5, 2002, pp. 729–736.

Halogenation of *N*-Substituted *p*-Quinonimines and *p*-Quinone Oxime Esters: II.* Chlorination and Bromination of 4-Aroyl(arylsulfonyl)oxyimino-2-methyl-2,5-cyclohexadienones**

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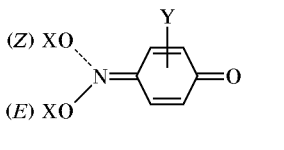
Received April 11, 2001

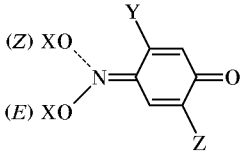
Abstract—Halogenation of 4-aroyl(arylsulfonyl)oxyimino-2-methyl-2,5-cyclohexadienones yields *Z*,*E*-isomeric 4-aroyl(arylsulfonyl)oxyimino-5,6-dihalo-2-methyl-2-cyclohexenones and (*E*)-4-aroyl(arylsulfonyl)oxyimino-5,6-dihalo-6-methyl-2-cyclohexenones. Further chlorination leads to formation of (*Z*,*E*)-4-aroyl(arylsulfonyl)oxyimino-2,5,6-trichloro-6-methyl-2-cyclohexenones.

In our previous communications [1, 2] we reported on the halogenation of alkyl-substituted 4-aroyl(arylsulfonyl)oxyimino-2,5-cyclohexadienones, which occurred at either of the quinoid C=C bonds. The substrates were compounds existing as a single isomer due to the presence of methyl group in the *ortho*-position with respect to the oxyimino group, which did not undergo *Z*,*E* isomerization. Further chlorination of 4-aroyl(arylsulfonyl)oxyimino-3-methyl(or 2,3-dimethyl, or 2-isopropyl-5-methyl)-2,5-cyclohexadienones containing chlorine in the quinoid ring gave chlorine addition products at the chlorine-substituted double bond [1]. In the chlorination of chlorine-substituted 4-aroyl(arylsulfonyl)oxyimino-3-methyl(or 2,3-dimethyl)-2,5-cyclohexadienones the addition occurred at either of the C=C bonds. The chlorine-substituted C=C bond was located *cis* with respect to the aroyl(arylsulfonyl)oxy group on the nitrogen. The chlorination of 2-chloro-4-(4-nitrobenzoyloxyimino)-6-isopropyl-3-methyl-2,5-cyclohexadienone can also involve either of the two quinoid double bonds, but the $C^2=C^3$ bond occupies *trans* position with respect to the substituent on the nitrogen. Taking into account that the *cis*-C=C bond is more reactive, no addition of chlorine at the $C^2=C^3$ bond should occur. However, chlorine molecule added at both $C^2=C^3$ and $C^5=C^6$ bonds of the substrate.

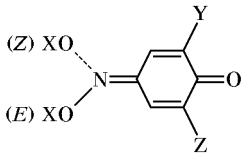
In the present work, we examined halogenation of 4-aroyl(arylsulfonyl)oxyimino-2-methyl-2,5-cyclohexadienones **I** which exist as *Z* and *E* isomers with a view to elucidate whether would the halogenation occur at the quinoid C=C bond having a chlorine atom attached thereto and occupying the *trans* position with respect to the substituent on the nitrogen. Hereinafter, we assume the *Z* isomer to have structure **A** where the aroyloxy or arylsulfonyloxy group is located *cis* relative to the quinoid double bond having a substituent. When substituents are present at both C=C bonds, *Z*,*E* isomers of **B** are defined with respect to the substituent located in the *ortho* position



A



B



C

X = ArCO, $ArSO_2$; **A**, **B**, Y, Z = Alk, Hlg; **C**, Y = Alk, Z = Hlg.

* For communication I, see [1].

** This study was financially supported by the EC INTAS Program (grant no. 00157-1999) and by the Ministry of Education and Science of Ukraine.

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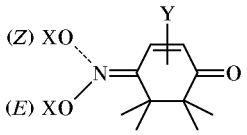
relative to the imino group. If the substituents occupy positions *2,6* or *3,5*, *Z,E* isomers are distinguished according to their rank. For 4-aroyl(arylsulfonyl)oxyimino-2-cyclohexenones **D**, regardless of the number, nature, and position of substituents, the *Z*-isomer is assumed to be that in which the *N*-aroyloxy or *N*-arylsulfonyloxy group is located *cis* with respect to the double C=C bond in the cyclohexene ring.



D

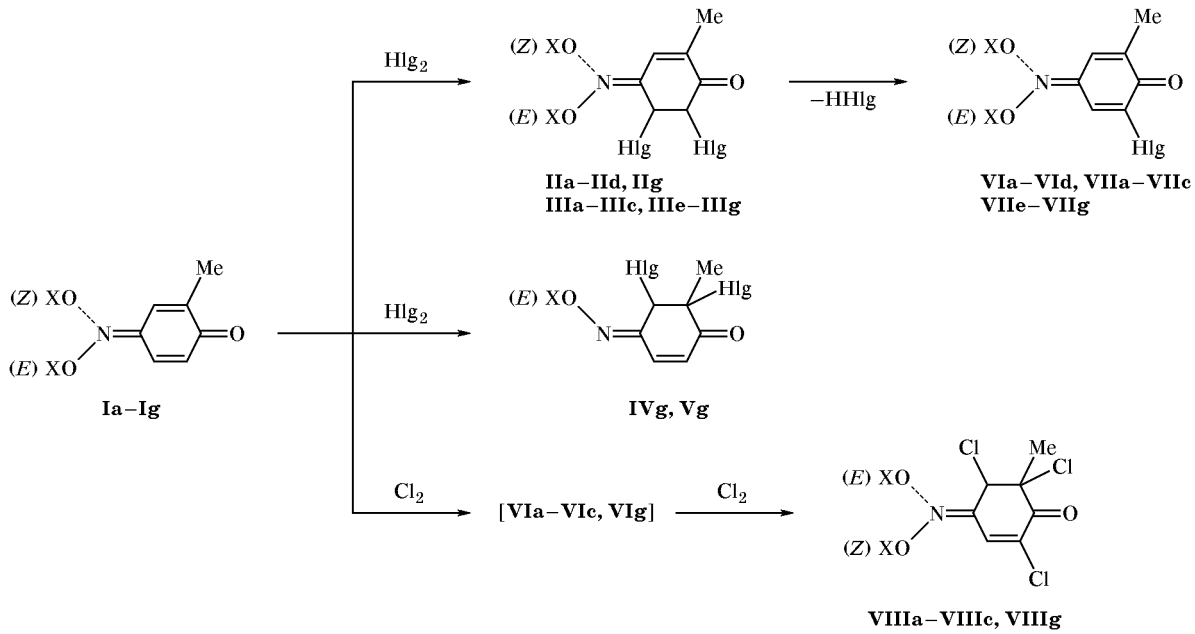
X = ArCO, $ArSO_2$; Y = Alk.

We previously studied [2, 3] addition of only one halogen molecule to 4-aroyloxyimino-2-methyl-2,5-cyclohexadienones. No further halogenation was examined. Scheme 1 illustrates processes involving addition of two halogen molecules to 4-aroyl(arylsulfonyl)oxyimino-2-methyl-2,5-cyclohexadienones **Ia**–**Ig**. The chlorination of compounds **Ia**–**Id** and **Ig** was carried out using gaseous chlorine and ethanol or DMF–acetic acid mixtures as solvent. The bromination of **Ia**–**Ic** and **Ie**–**Ig** was effected with bromine in acetic acid. The first halogenation stage (as in [2, 3]) occurs at the unsubstituted C=C bond of the quinoid ring, yielding either *Z* or *E* isomers and in some cases *Z,E*-isomeric mixtures of 4-aroyl(arylsulfonyl)oxyimino-5,6-dihalo-2-methyl-2-cyclohexenones **IIa**–**IId**, **IIg**, **IIIa**–**IIIc**, and **IIIe**–**IIIg**. Previously [3], only the *E* isomers of **II** were isolated in the chlorination of **I**. We were the first to obtain halogen addition products at the methyl-substituted double bond of **Ig**, 4-(4-nitrophenylsulfonyl)oxyimino-5,6-dihalo-6-methyl-2-cyclohexenones **IVg** and **Vg**. It should be noted that this reaction occurs only with the *Z* isomer of **Ig** in which the $C^2=C^3$ bond is activated due to *cis* arrangement of the 4-$NO_2C_6H_4SO_2O$ group on the nitrogen. The effect of the substituent on the nitrogen on the reactivity of quinoid double bonds was revealed for the first time in [4], but no clear explanation was proposed.

Compounds **IVg** and **Vg** do not undergo dehydrochlorination on treatment with triethylamine in chloroform or with sodium acetate in acetic acid, which is consistent with the dehydrohalogenation regioselectivity rules formulated in [5].

Dehydrohalogenation of compounds **II** and **III** yields 4-aroyl(arylsulfonyl)oxyimino-6-halo-2-methyl-2,5-cyclohexadienones **VIa**–**VId**, **VIIa**–**VIIc**, and **VIIe**–**VIIg**. As expected, halogen atom is abstracted exclusively from the *ortho*-position with respect to the carbonyl group.

Scheme 1.



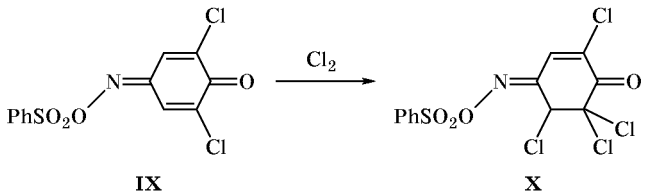
X = C_6H_5CO (**a**), 4-$NO_2C_6H_4CO$ (**b**), $C_6H_5SO_2$ (**c**), 4-$ClC_6H_4SO_2$ (**d**), 4-$CH_3C_6H_4SO_2$ (**e**), 3-$NO_2C_6H_4SO_2$ (**f**), 4-$NO_2C_6H_4SO_2$ (**g**); **II**, **IV**, **VI**, Hlg = Cl; **III**, **V**, **VII**, Hlg = Br.

By chlorination of compounds **Ia**–**Ic** and **Ig** under more severe conditions (in DMF–AcOH, 3:1) we obtained products of addition of two chlorine molecules, 4-aroyl(arylsulfonyl)oxyimino-2,5,6-trichloro-6-methyl-2-cyclohexenones **VIIIa**–**VIIIc** and **VIIIg**. Obviously, the reactions involves intermediate formation of the corresponding 4-aroyl(arylsulfonyl)oxyimino-6-chloro-2-methyl-2,5-cyclohexadienes **VI**. It should be noted that, as well as in the halogenation of **Ig**, chlorine addition to compounds **VI** occurs mainly at the methyl-substituted C=C bond of the quinoid ring of the *Z* isomer in which this C=C bond is located *cis* with respect to the XO substituent on the nitrogen. Addition at the corresponding bond of *E* isomer was observed only in the chlorination of oxime ester **Ia**, and the fraction of the product was only 15% of the overall amount of the chlorination products (according to the ^{1}H NMR data). No chlorine addition products at the chlorine-substituted C=C bond were detected.

Thus the results of our previous studies [1–3] and those obtained in the present work suggest that the direction of halogenation depends not only on the orientation of XO group on the nitrogen (*cis* or *trans*) and the size of substituents at the C=C bond but also on the nature of these substituents (donor or acceptor) and their position with respect to the imino group (*ortho* or *meta*). In other words, electron density distribution in the quinoid ring is an important factor among those governing halogen addition process.

Finally, we effected chlorination of 2,6-dichloro-4-phenylsulfonyloxyimino-2,5-cyclohexadienone (**IX**) (Scheme 2). Previously, we failed to add chlorine molecule to 4-arylsulfonyloxyimino-2,6-dichloro-2,5-cyclohexadienones [6]. This reaction attracts interest in comparison with the chlorination of compounds **I**, which involves intermediate formation of 4-aroyl(arylsulfonyl)oxyimino-6-chloro-2-methyl-2,5-cyclohexadienones **VI**. The latter take up chlorine only at the $C^2=C^3$ bond to give both *Z* and *E* isomers of **VIII**. From compound **IX** (Scheme 2) we obtained only the corresponding *E* isomer, 2,5,6,6-tetrachloro-4-phenylsulfonyloxyimino-2-cyclohexenone (**X**), i.e., the reaction occurs exclusively at the *cis*-C=C bond.

Scheme 2.



IX **X**

The structure of compounds **II**–**VIII** was proved by elemental analysis (Table 1) and ^{1}H NNR spectroscopy (Table 2). The ^{13}C NMR spectrum of compound **IIIc** was also recorded. The 3-H signal in the ^{1}H NMR spectra of **II** and **III** is observed at δ 7.24–7.47 ppm (*Z* isomers) or δ 6.73–7.16 ppm (*E* isomers). It is split into a quartet due to coupling with the methyl protons; its position is consistent with its location in the *ortho* position with respect to the C=N group. The 5-H and 6-H signals are doublets of doublets and doublets at δ 4.92–5.74 and 4.43–4.84 ppm, respectively. Their chemical shifts indicate that these protons are attached to sp^3-hybridized carbon atoms. The 5-H proton is coupled with 6-H and 3-H, and 6-H, only with 5-H. The ^{13}C NMR spectrum of **IIIc** contains upfield signals from sp^3-hybridized carbon atoms (CHBr) at δ_C 43.55 and 44.79 ppm. The ^{1}H NMR spectra of **IIa** and **IIIa** were reported in [2, 3].

In the ^{1}H NMR spectra of **IVg** and **Vg** the 2-H proton appears as a doublet at δ 6.45 ppm, the 3-H signal is a doublet of doublets at δ 6.90–6.94 ppm, and that from 5-H is a doublet at δ 5.50–5.70 ppm. The positions of these signals are consistent with the assigned structure. The coupling constants between 2-H and 3-H and between 3-H and 5-H are equal to 10.5 and 1.8 Hz, respectively. The 3-H signal of **VI** and **VII** is a quartet at δ 7.46–7.61 ppm (*Z* isomers) or δ 6.90–7.31 ppm (*E* isomers); the signal from 5-H is located at δ 7.27–7.87 ppm (*Z* isomers) or δ 7.75–8.20 ppm (*E* isomers). It is split into a doublet due to coupling with 3-H. Compounds **VIII** show in the ^{1}H NMR spectra doublet signals at δ 7.14–7.49 and 7.82 ppm for the *Z* and *E* isomers, respectively. The 5-H signal is a doublet at δ 5.49–5.62 (*Z*) or 5.28 ppm (*E* isomer). The coupling constants range from 1.5 to 1.8 Hz. The ^{1}H NMR spectrum of **X** contains two doublets typical of hydrogen atoms attached to sp^2- and sp^3-hybridized carbon atoms of the *E* isomer.

The IR spectra of oxime esters **VIa**–**VId**, **VIIa**–**VIIc**, and **VIIe**–**VIIg** are characterized by the presence of absorption bands in the regions 1660–1655, 1610–1585, and 1545–1475 cm^{-1}, which belong to stretching vibrations of the C=O, C=C, and C=N bonds, respectively. The carbonyl absorption band of compounds **II**–**V** and **VIII** has a higher frequency; and their IR spectra contain bands at 1710–1685 (C=O), 1630–1600 (C=C), and 1600–1500 cm^{-1} (C=N).

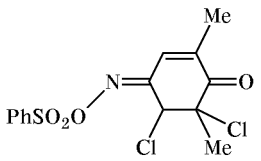
On the basis of the data given in [4, 7, 8] and coupling constants in the ^{1}H NMR spectra we presumed [3] *trans*-diaxial arrangement of the chlorine

Table 1. Melting points and elemental analyses of compounds **IIa**–**IId**, **IIIb**, **IIIc**, **IIIe**, **VIb**, **VIc**, **VIIb**, **VIIc**, and **VIIIa**–**VIIIc**[a]

Comp. no.	mp, °C	Found, %		Formula	Calculated, %	
		Hlg	N		Hlg	N
E-**IIa**	212	22.68, 22.79	–	$C_{14}H_{11}Cl_2NO_3$	22.72	–
E-**IIb**	138	19.80, 19.97	–	$C_{14}H_{10}Cl_2N_2O_5$	19.85	–
Z-**IIc**	122	20.42, 20.50	–	$C_{13}H_{11}Cl_2NO_4S$	20.36	–
Z-**IId**	151	27.65, 27.83	–	$C_{13}H_{10}Cl_3NO_4S$	27.80	–
Z-**IIIb**[b]	164	35.65, 35.88	6.30, 6.38	$C_{14}H_{10}Br_2N_2O_5$	35.83	6.28
Z-**IIIc**	113	36.63, 36.83	3.27, 3.32	$C_{13}H_{11}Br_2NO_4S$	36.56	3.20
Z-**IIIe**	119	35.39, 35.40	3.01, 3.20	$C_{14}H_{13}Br_2NO_4S$	35.42	3.10
E-**VIb**	233 (decomp.)	11.01, 11.29	–	$C_{14}H_9ClN_2O_5$	11.06	–
E-**VIc**	134	11.11, 11.32	–	$C_{13}H_{10}ClNO_4S$	11.37	–
Z-**VIIb**	220 (decomp.)	21.63, 21.74	7.47, 7.58	$C_{14}H_9BrN_2O_5$	21.88	7.67
E-**VIIb**	230 (decomp.)	21.60, 21.72	7.76, 7.88	$C_{14}H_9BrN_2O_5$	21.88	7.67
Z-**VIIc**	140	22.25, 22.37	3.98, 4.06	$C_{13}H_{10}BrNO_4S$	22.43	3.93
E-**VIIIa**	130	30.53, 30.75	4.08, 4.24	$C_{14}H_{10}Cl_3NO_3$	30.69	4.04
E-**VIIIb**	211	27.01, 27.12	7.03, 7.05	$C_{14}H_9Cl_3N_2O_5$	27.16	7.15
E-**VIIIc**	135	27.93, 28.14	3.76, 3.97	$C_{13}H_{10}Cl_3NO_4S$	27.80	3.66

[a] The melting points and elemental analyses are given for individual *Z* and *E* isomers.
[b] The data for the *E* isomer are given in [2].

atoms attached to sp^3-hybridized carbon atoms in cyclohexene structures obtained by chlorination of *p*-quinone oxime esters. This assumption was confirmed by X-ray diffraction data for the HCCl−CClH fragment [1]. In the present work we obtained cyclohexene structures **IV**, **V**, and **VIII** which possess an HCCl−C(CH_3)Cl fragment. In order to determine its structure (whether the chlorine atoms therein are also *trans*-diaxial or not) we performed X-ray analysis of a single crystal of compound **VIIIc**. The results showed that the Cl^2 and Cl^3 atoms in **VIIIc** occupy the axial positions with *trans* arrangement with respect to each other and that the 3-H hydrogen atom and 2-CH_3 group are nearly equatorial. The sp^3-hybridized C^5 and C^6 atoms deviate by –0.291 and +0.284 Å, respectively, from the plane formed by the C^1, C^2, C^3, and C^4 atoms. In keeping with the ^{1}H NMR data, molecule **VIIIc** has *E* configuration where the phenylsulfonyloxy group is located *trans* relative to the cyclohexene C=C bond (Fig. 1).



XI

Analogous results were obtained for structurally related 5,6-dichloro-2,6-dimethyl-4-phenylsulfonyloxyimino-2-cyclohexenone (**XI**) which was synthesized previously by chlorination of 2,6-dimethyl-4-phenylsulfonyloxyimino-2,5-cyclohexadienone [9]. The $C^1C^2C^3C^4$ fragment in **XI** is planar within 0.001 Å. The C^5, C^6, Cl^1, and Cl^2 atoms are disordered by two positions, presumably because of the lack of stereoselectivity in the chlorine addition at the quinoid C=C bond. Two conformers **XIA** and **XIB** are simultaneously present in a unit cell, their populations being equal to 68 and 32%, respectively (Fig. 2). The deviations of the C^5 and C^6 atoms of conformer

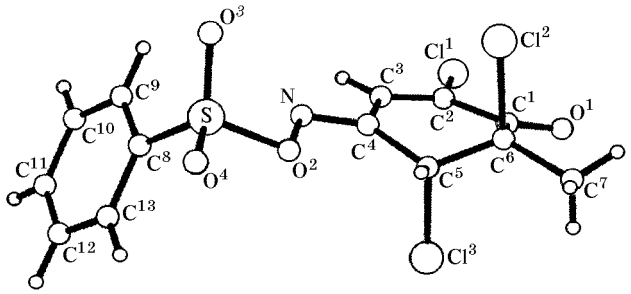


Fig. 1. Structure of the molecule of 2,5,6-trichloro-6-methyl-4-phenylsulfonyloxyimino-2-cyclohexenone (**VIIIc**) according to the X-ray diffraction data.

Table 2. ^{1}H NMR spectra of compounds **IIa**–**IId**, **IIg**, **IIIa**–**IIIc**, **IIIe**–**IIIg**, **IVg**, **Vg**, **VIa**, **VIc**, **VId**, **VIIb**, **VIIc**, **VIIe**–**VIIg**, **VIIIa**–**VIIIc**, **VIIIg** and **X** in DMSO-d_6

Comp. no.	Isomer (%)	Chemical shifts δ, ppm					J, Hz
		2-H, 2-Me	3-H	5-H	6-H, 6-Me	X	
IIa	*E* (100)	2.12 d	7.16 q	5.64 d.d	4.51 d	7.30–8.12 m	$J_{5,6}$ = 2.7, $J_{3,Me}$ = 1.2
IIb	*E* (100)	2.14 d	7.16 q	5.62 d.d	4.53 d	8.29–8.41 d.d	$J_{5,6}$ = 2.7, $J_{3,Me}$ = 1.2
IIc	*Z* (100)	2.06 d	7.31 q	4.95 d.d	4.48 d	7.56–8.04 m	$J_{5,6}$ = 3.2, $J_{3,Me}$ = 1.8
IId[a]	*Z* (100)	2.08 d	7.30 q	4.93 d.d	4.51 d	7.55–7.97 d.d	$J_{5,6}$ = 3.3, $J_{3,Me}$ = 1.2
IIg	*Z* (33)	2.05 d	7.31 q	4.92 d.d	4.52 d	8.21–8.46 d.d	$J_{5,6}$ = 3.0, $J_{3,Me}$ = 1.8
	E (33)	2.09 d	6.80 q	5.47 d.d	4.43 d		
IIIa	*Z* (17)	2.17 d	7.47 q	5.46 d.d	4.83 d	7.52–8.15 m	$J_{5,6}$ = 2.4, $J_{3,Me}$ = 1.8
	E (83)	2.13 d	7.12 q	5.74 d.d	4.71 d		$J_{5,6}$ = 3.0, $J_{3,Me}$ = 1.5
IIIb	*Z* (100)	2.19 d	7.42 q	5.44 d.d	4.84 d	8.29–8.41 d.d	$J_{5,6}$ = 3.0, $J_{3,Me}$ = 1.5
	E (100)	2.15 d	7.11 q	5.71 d.d	4.72 d	8.30–8.42 d.d	$J_{5,6}$ = 2.4, $J_{3,Me}$ = 1.5
IIIc	*Z* (94)	2.07 d	7.28 q	5.01 d.d	4.70 d	7.56–8.02 m	$J_{5,6}$ = 2.7, $J_{3,Me}$ = 1.8
	E (6)	2.04 d	6.78 q	5.56 d.d	4.60 d		
IIIe	*Z* (95)	2.10 d	7.26 q	5.09 d.d	4.69 d	7.27–7.90 d.d,	$J_{5,6}$ = 2.8, $J_{3,Me}$ = 2.0
	E (5)	2.00 d	6.79 q	5.57 d.d	4.60 d	2.49 s (CH_3)	
IIIf	*Z* (79)	2.11 d	7.24 q	5.09 d.d	4.71 d	7.79–8.86 m	$J_{5,6}$ = 2.8, $J_{3,Me}$ = 1.9
	E (21)	2.01 d	6.73 q	5.53 d.d	4.62 d		
IIIg	*Z* (71)	2.11 d	7.26 q	5.08 d.d	4.72 d	8.20–8.45 d.d	$J_{5,6}$ = 3.0, $J_{3,Me}$ = 1.5
	E (20)	2.06 d	6.74 q	5.57 d.d	4.61 d		
IVg	*E* (34)	6.45 d	6.94 d.d	5.50 d	1.86 s	8.21–8.46 d.d	$J_{2,3}$ = 10.5, $J_{3,5}$ = 1.8
Vg	*E* (9)	6.45 d	6.90 d.d	5.70 d	2.04 s	8.20–8.45 d.d	$J_{2,3}$ = 10.5, $J_{3,5}$ = 1.8
VIa	*Z* (17)	2.21 d	7.72 q	7.62 d	–	7.54–8.16 m	$J_{3,Me}$ = 1.5, $J_{3,5}$ = 2.4
	E (83)	2.16 d	7.32 q	7.96 d	–		
VIc	*Z* (64)	2.13 d	7.47 q	7.28 d	–	7.58–8.04 m	$J_{3,Me}$ = 1.2, $J_{3,5}$ = 2.4
	E (36)	2.08 d	6.98 q	7.78 d	–		
VId	*Z* (47)	2.14 d	7.46 q	7.27 d	–	7.56–7.98 d.d	$J_{3,Me}$ = 1.2, $J_{3,5}$ = 2.4
	E (53)	2.08 d	6.97 q	7.96 d	–		
VIIb	*Z* (36)	2.24 d	7.61 q	7.87 d	–	8.32–8.43 d.d	$J_{3,5}$ = 2.4[a]
	E (64)	2.18 d	7.31 q	8.20 d	–		
VIIc	*Z* (96)	2.13 d	7.48 q	7.54 d	–	7.58–8.04 m	$J_{3,Me}$ = 1.5, $J_{3,5}$ = 2.4
	E (4)	2.08 d	6.98 q	7.75 d	–		
VIIe	*Z* (78)	2.13 d	7.47 q	7.53 d	–	7.36–7.92 d.d,	$J_{3,Me}$ = 1.7, $J_{3,5}$ = 2.5
	E (22)	2.02 d	6.95 q	8.08 d	–	2.47 s (CH_3)	
VIIf	*Z* (77)	2.16 d	7.47 q	7.52 d	–	8.32–8.88 m	$J_{3,Me}$ = 1.5, $J_{3,5}$ = 2.4
	E (23)	2.10 d	6.90 q	8.00 d	–		
VIIg	*Z* (75)	2.15 d	7.46 q	7.51 d	–	8.22–8.45 d.d	$J_{3,Me}$ = 1.8, $J_{3,5}$ = 2.5
	E (25)	2.09 d	6.95 q	8.05 d	–		
VIIIa	*E* (85)	–	7.49 d	5.62 d	2.01 s	7.54–8.16 m	$J_{3,5}$ = 1.5
	E (15)	–	7.82 d	5.28 d	2.02 s		
VIIIb	*E* (100)	–	7.49 d	5.59 d	2.01 s	8.29–8.43 d.d	$J_{3,5}$ = 1.5
VIIIc	*E* (100)	–	7.15 d	5.49 d	1.90 s	7.53–8.01 m	$J_{3,5}$ = 1.7
VIIIg	*E* (100)	–	7.14 d	5.49 d	1.93 s	8.20–8.46 d.d	$J_{3,5}$ = 1.8
X	*E* (40)	–	7.22 d	5.81 d	–	7.60–8.07 m	$J_{3,5}$ = 1.8

[b] We failed to determine $J_{3,Me}$.

Table 3. Chlorination of quinone oxime esters **Ia**–**Id** and **Ig**

Initial compound	Solvent	c_I, M	Temperature, °C	Products (isomer fraction, %)[a]
Ia	DMF–AcOH (3:1)	0.6	40–50	**IIa** (*E*, 100)[b], **VIIIa** (*Z*, 100)[c]
	DMF–AcOH (3:1)	0.2	40–50	**VIIIa** (*E*, 85; *Z*, 15)[d]
Ib	DMF–AcOH (1:1)	0.3	45	**IIb** (*E*, 100)[d]
	DMF–AcOH (3:1)	0.5	30–40	**VIIIb** (*E*, 100)[e]
Ic	DMF–AcOH (1:1)	0.5	40	**IIc** (*Z*, 100)[d]
	DMF–AcOH (3:1)	0.4	60	**VIIIc** (*E*, 100)[c]
	EtOH	0.4	20	**VIc** (*Z*, 64; *E*, 36)[e]
Id	DMF–AcOH (1:1)	0.3	60	**IId** (*Z*, 100)[d]
	EtOH	0.3	25	**VId** (*Z*, 47; *E*, 53)[e]
Ig	DMF–AcOH (5:1)	0.3	60	**IIg** (*Z*, 33; *E*, 33), **IVg** (*E*, 34)[d]
	DMF–AcOH (3:1)	0.5	50	**IIg** (*Z*, 10), **IVg** (*E*, 22), **VIIIg** (*E*, 68)[d]

[a] According to the ^{1}H NMR data.
[b] The product precipitated immediately after chlorination.
[c] The product was isolated by adding water to the filtrate.
[d] The product was isolated by adding water to the reaction solution.
[e] The product precipitated after 3 days.

XIA from the mean-square plane formed by the C^1, C^2, C^3, and C^4 atoms are +0.252 and –0.434 Å, respectively; the corresponding values for **XIB** are –0.327 and +0.113 Å. In both conformers the chlorine atoms occupy axial positions and are arranged *trans* with respect to each other. The hydrogen atom and methyl group are nearly equatorial. Molecule **XI** has *E* configuration with the $C_6H_5SO_2O$ group located *trans* relative to the cyclohexenone double bond.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer in KBr. The ^{1}H NMR spectra were measured on a Varian VXR-300 instrument at 300 MHz using $CDCl_3$ as solvent and TMS as internal reference. The ^{13}C NMR spectrum of compound **IIIc** was obtained on the same instrument at 75.4 MHz in $CDCl_3$ relative to TMS. The reaction mixtures were analyzed by TLC on Silufol UV-254 plates using benzene–ethyl acetate (10:1) as eluent; spots were visualized by UV irradiation.

X-Ray diffraction data for single crystals of **VIIIc** and **XI** (monoclinic) were obtained at room temperature using an Enraf–Nonius CAD-4 four-circle automatic diffractometer [λMoK_α irradiation for **VIIIc** and λCuK_α for **XI**, graphite monochromator, scan rate ratio $\omega/2\Theta$ 1.2]. The parameters of unit cells and crystal orientation matrices were determined from 22 reflections with $12 < \Theta < 13$ for compound **VIIIc** and $28 < \Theta < 30$ for **XI**. The structures were solved by the direct method and were refined by the least-squares procedure in full-matrix anisotropic approximation using SHELXS and SHELXL-93 software [10, 11]. All hydrogen atoms were visualized objectively but were included in the calculations with fixed thermal and positional parameters.

4-Aroyl(arylsulfonyl)oxyimino-2-methyl-2,5-cyclohexadienones **Ia**–**Ig** were synthesized by acylation of 2-methyl-1,4-benzoquinone 4-oxime with the corresponding aroyl or arenesulfonyl chlorides in diethyl ether in the presence of triethylamine, following the procedure reported in [12]. Newly synthesized quinone oxime esters **Ic**–**Ig** were mixtures of *Z* and

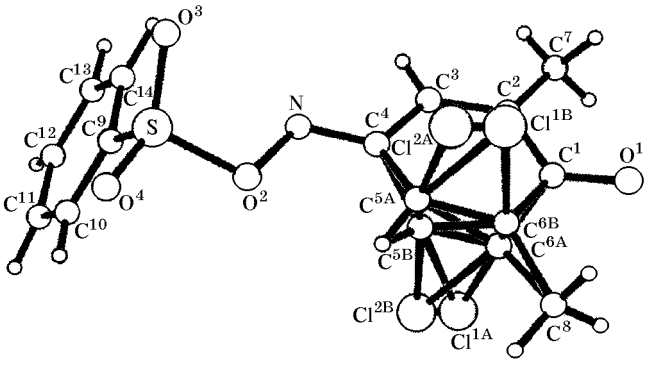


Fig. 2. Structure of the molecule of 5,6-dichloro-2,6-dimethyl-4-phenylsulfonyloxyimino-2-cyclohexenone (**XI**) according to the X-ray diffraction data.

E isomers; according to the data of elemental analysis, they contain no products of different elemental composition.

Chlorination of quinone oxime esters Ia–Id and Ig (Table 3). Chlorine was passed at a flow rate of 15–20 ml/min through a 0.2–0.6 M solution of compound **Ia**–**Id** or **Ig** in 5 ml of appropriate solvent until saturation. The product was filtered off and recrystallized from acetic acid.

Chlorination of 2,6-dichloro-4-phenylsulfonyloxyimino-2,5-cyclohexadienone (IX). A solution of 1.4 mmol of compound **IX** was dissolved in 3 ml of DMF, and the solution was saturated with chlorine at a flow rate of 15–20 ml/min (60°C). The precipitate was filtered off and recrystallized from acetic acid. The product contained 60% of unchanged initial compound **IX** and 40% of *E*-**X** (according to the ^{1}H NMR data.

Bromination of quinone oxime esters Ia–Ic and Ie–Ig. A 5 M solution of bromine in acetic acid was added dropwise under vigorous stirring to 5 ml of a 0.2 M solution of compound **Ia**–**Ic** or **Ie**–**Ig**, the ratio **I**:Br_2 being 1:3. The mixture was heated until the initial oxime ester dissolved. It was then cooled to room temperature and poured onto ice, and the precipitate was filtered off and recrystallized from glacial acetic acid. Compounds **IIIa**–**IIIc**, **IIIe**, and **IIIf** were thus obtained. In the bromination of **Ig** we isolated a mixture of products **IIIg** and **Vg**.

Dehydrohalogenation of compounds IIa–IId, IIIa, IIIc, and IIIe–IIIg. *a.* Triethylamine, 0.10–0.15 ml, was added to a solution of 1 mmol of compound **IIa**, **IIb**, or **IIIe**–**IIIg** in a minimal amount of chloroform, and the mixture was heated to the boiling point. It was then cooled to room temperature, and the precipitate was filtered off, washed with a small amount of acetic acid and water, and recrystallized from glacial acetic acid.

b. Sodium acetate, 1 mmol, was added to a solution of 1 mmol of compound **IIc**, **IId**, or **IIIa**–**IIIc** in a minimal amount of acetic acid, and the mixture was refluxed for several minutes. It was then cooled, and the product was filtered off and recrystallized from glacial acetic acid.

REFERENCES

1. Avdeenko, A.P., Glinyanaya, N.M., Konovalova, S.A., Shishkina, S.V., and Goncharova, S.A., *Russ. J. Org. Chem.*, 2002, vol. 38, no. 5, pp. 683–691.
2. Avdeenko, A.P., Glinyanaya, N.M., and Pirozhenko, V.V., *Russ. J. Org. Chem.*, 1995, vol. 31, no. 10, pp. 1380–1385.
3. Avdeenko, A.P., Glinyanaya, N.M., and Pirozhenko, V.V., *Russ. J. Org. Chem.*, 1996, vol. 32, no. 1, pp. 85–89.
4. Baldwin, J.E. and Norris, R.K., *J. Org. Chem.*, 1981, vol. 46, no. 4, pp. 697–703.
5. Avdeenko, A.P., Zhukova, S.A., and Konovalova, S.A., *Russ. J. Org. Chem.*, 2001, vol. 37, no. 3, pp. 382–387.
6. Avdeenko, A.P. and Glinyanaya, N.M., *Russ. J. Org. Chem.*, 1995, vol. 31, no. 11, pp. 1507–1513.
7. Avdeenko, A.P., Velichko, N.V., and Romanenko, E.A., *Zh. Org. Khim.*, 1991, vol. 27, no. 11, pp. 2350–2361.
8. Avdeenko, A.P., Glinyanaya, N.M., and Pirozhenko, *Zh. Org. Khim.*, 1993, vol. 29, no. 7, pp. 1402–1411.
9. Avdeenko, A.P., Zhukova, S.A., Glinyanaya, N.M., and Konovalova, S.A., *Russ. J. Org. Chem.*, 1999, vol. 35, no. 4, pp. 560–571.
10. Sheldric, G.M., *SHELXS-86. Program for the Solution of Crystal Structures*, Gottingen: Univ. of Gottingen, 1986.
11. Sheldric, G.M., *SHELXL-93. Program for the Refinement of Crystal Structures*, Gottingen: Univ. of Gottingen, 1993.
12. Titov, E.A. and Burmistrov, S.I., *Ukr. Khim. Zh.*, 1960, vol. 26, no. 6, pp. 744–749.